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Polarographic Investigations of Some Metal Monocarboxylato Complexes. IV. Influence of Monocarboxylic Acid on the Half-wave Potential of Metal Ions

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The influence of monocarboxylic acids (formic, acetic and butyric) on the half-wave potential of metal ions (lead, cadmium, copper(II) and thallium(I)) in the monocarboxylate buffer was established. Since this influence is opposite to that of complex formation, it is necessary to investigate the monocarboxylate complexes in buffers with a constant acid concentration rather than in buffers with a constant salt-acid ratio. The positive shift of the half-wave potential with the increase of the monocarboxylic acid concentration in the buffer is caused by the change of the liquid junction potential, by the change of the activity coefficient of the ion and by the change of the viscosity of the solution.

The polarographic determination of the stability constant of a complex is based on the measurement of the change of the half-wave potential ($E_{1/2}$) and the diffusion current (i_d) of the metal ion in the presence of the complex forming agent.[1] By complex formation the half-wave potential of the metal ion is shifted towards more negative values. For cases where in the solution an equilibrium is obtained between complexes with a different number of ligands, DeFord and Hume[2] have established the following relation between the half-wave potential and the cumulative stability constant (β_j) of the complexes in equilibrium:

$$(E_{1/2})_s - (E_{1/2})_c = \frac{0.059}{n} \log \frac{I_c}{I_s} + \frac{0.059}{n} \log \sum_o^j \beta_j [L]^j$$

or:

$$\sum_o^j \beta_j [L]^j = \text{antilog} \left\{ 16.95\, n\, [(E_{1/2})_s - (E_{1/2})_c] + \log \frac{I_s}{I_c} \right\}$$

where $(E_{1/2})_s$ is the half-wave potential of the *free* metal ion, $(E_{1/2})_c$ that of the complex ion, I_s and I_c are the analogous diffusion current constants, [L] is the concentration of the ligand, j is the number of ligands bonded to the central metal ion and β_j is the cumulative stability constant of the complex. Since the expression on the left side of the equation is a function of the concentration, *i.e.*:

$$\sum_o^j \beta_j [L]^j = 1 + \beta_1 [L] + \beta_2 [L]^2 + \ldots + \beta_j [L]^j = F([L]),$$

the consecutive stability constant can be obtained graphically by plotting the funkction $F([L])$ against ligand concentration and by extrapolating to zero ligand concentration.

Therefore, the determination of the stability constant of a complex by the polarographic method consists in the determination of the half-wave potentials and the diffusion currents of the *free* and complex metal ion. The principal condition for such measurements is the »polarographic« reversibility of the electrode process.[1] The half-wave potential of the *free* metal ion can be determined experimentally either by direct measurements in an indifferent electrolyte of the same ionic strength but without the ligand, or, if it is possible, graphically by extrapolation to zero ligand concentration. The same applies to the diffusion current or diffusion current constant. Besides, it is possible to calculate the half-wave potential of the free ion from the standard potential of the metal, its solubility in mercury and its affinity for mercury, as was shown by J. J. Lingane and M. von Stackelberg.[1]

In the solution of the metal ion, which contains the monocarboxylate ion as ligand (formate, acetate, propionate and butyrate), an equilibrium exists between a series of monocarboxylato complexes, as was found by different methods. E. A. Burns and D. M. Hume[3] have investigated the lead acetato complexes by the polarographic method, the potentiometric method and the solubility method, using a constant ionic strength 2 and a constant, relatively high, concentration of acetic acid of 2 *M* in the acetate buffer. Under the same conditions I. Filipović *et al.*[4-6] have investigated by the polarographic method the formato, acetato, propionato and butyrato complexes of lead, cadmium, copper and zinc. H. M. Hershenson *et al.*[7] have investigated by the polarographic method the formato complexes of cadmium, copper, lead, thallium and zinc, using constant ionic strength 2, but with a constant formic acid concentration of only 0.01 *M* in the buffer. Besides, these authors have decreased the diffusion potential to a minimum by application of a quinhydrone reference electrode. D. Cozzi and S. Vivarelly[8] have studied the polarographic characteristics of indium in an acetate buffer of constant *p*H 4.64. H. Matsuda, Y. Ayabe and K. Adachi[9] have also determined the stability constants of the zinc acetato complexes by polarographic investigations in acetate buffers of constant *p*H 6.0.

E. A. Burns and D. N. Hume[3] have investigated the influence of the acetic acid concentration in the acetate buffer on the half-wave potential of lead and have found that with an increase of the acid concentration it is shifted to more positive values. The authors have ascribed this phenomenon to the hydrolysis of the lead acetato complexes at lower acetic acid concentrations, in spite of the fact that this phenomenon was much more pronounced in buffer solutions of a high acetic acid concentration. Our investigations have shown that the same phenomenon occurs in all other monocarboxylic buffers and with all other investigated metal ions (copper, cadmium and zinc).

For this reason a systematic polarographic study of metal ions in monocarboxylate buffer solutions of a constant acid-salt ratio was carried out, as well as in buffer solutions of a constant acid concentration.

EXPERIMENTAL AND RESULTS

The measurements have been performed with a polarographic apparatus described in previous papers[4-6]. The same applies to the half-wave potential and diffusion current determination, as well as to the preparation of solutions. By the addition of sodium perchlorate the ionic strength of the solutions was kept at a constant value 2. The ligand concentration was calculated from the concentration of the monocarboxylate and monocarboxylic acid, using the dissociation constant of the acid. The electrode processes of the investigated ions (cadmium, lead and copper) in monocarboxylic buffers were reversible, *i.e.* the ratio $\Delta E_{d.e.}/\Delta \log [(i_d\text{-}i)/i]$ was about 30 mV. The relative coefficients of viscosity (against water) were determined by means of an Ostwald viscosimeter.[10]

Buffers of Constant Acid-Salt Ratio

The results for some metal ions in a number of monocarboxylic buffers of constant acid-salt ratio (5 : 1, 10 : 1, 50 : 1, 100 : 1 and 200 : 1) are given graphically in Figs. 1—3. The ionic strength of the buffers was kept at the constant value 2. All ions investigated (lead, cadmium and copper) gave analogous results in all monocarboxylic buffers used (formate, acetate and butyrate). As can be seen from Fig. 1, only in the buffer 5 : 1 the half-wave potential of cadmium is shifted to more negative values with the increase of the formate concentration, as corresponds to the formation of complexes. In buffers of a higher formic acid concentration, in spite of the increase in ligand concentration and an appproximately constant *p*H, the half-wave is shifted to more positive values in proportion to the acid concentration in the buffer. The same is true for the acetic and butyric acid, as can be seen from Figs. 2 and 3. Lead and copper give analogous results as can be seen from Figs. 4 and 5 for formic acid and acetic acid respectively. Consequently the shift of the half-wave potential of cadmium (lead and copper) to more positive values with increasing acid concentration is not caused by the inhibition of the formation of mixed hydroxo complexes, because the shift is particularly pronounced in very acid buffers. In such buffers the hydrolysis of the metal monocarboxylato complexes does not occur at all. It is obvious that the monocarboxylic acid alone is responsible for the positive shift of the half-wave potential and the higher its concentration in the buffer, the greater its influence.

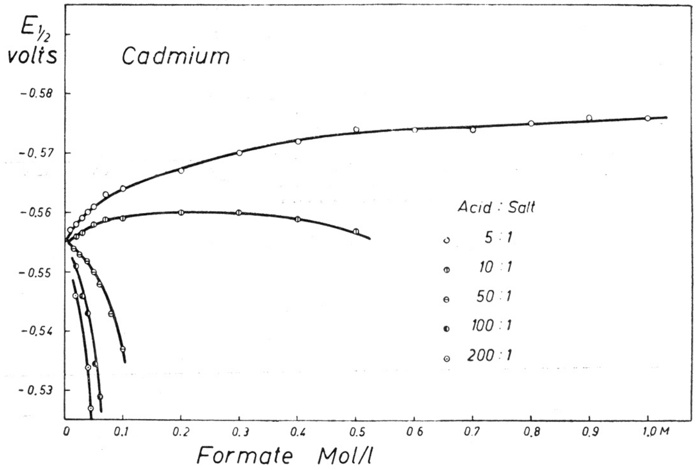


Fig. 1 **Half-wave potential of cadmium *versus* formate concentration in buffers of acid-salt ratio: 5 : 1, 10 : 1, 50 : 1, 100 : 1, 200 : 1.**

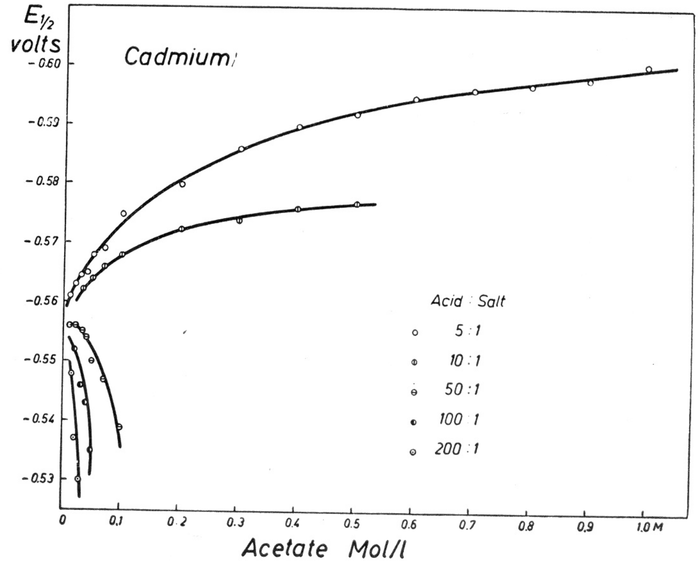


Fig. 2 Half-wave potential of cadmium *versus* acetate concentration in buffers of acid-salt ratio: 5 : 1, 10 : 1, 50 : 1, 100 : 1 and 200 : 1.

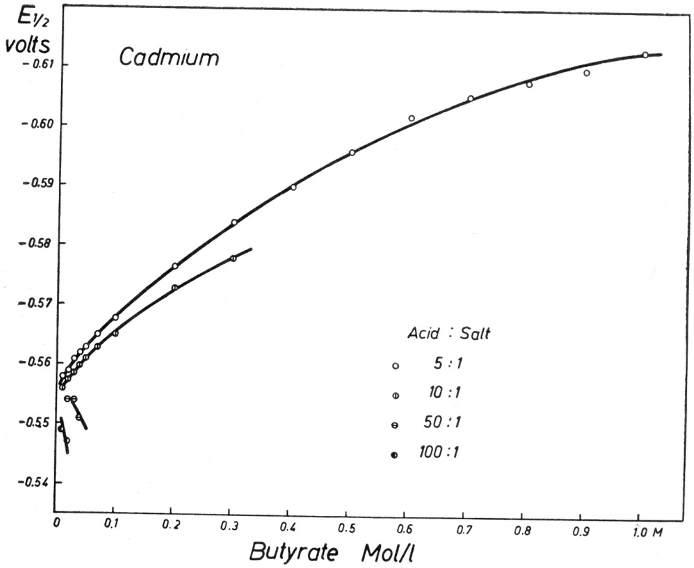


Fig. 3 Half-wave potential of cadmium *versus* butyrate concentration in buffers of acid-salt ratio: 5 : 1, 10 : 1, 50 : 1 and 100 : 1.

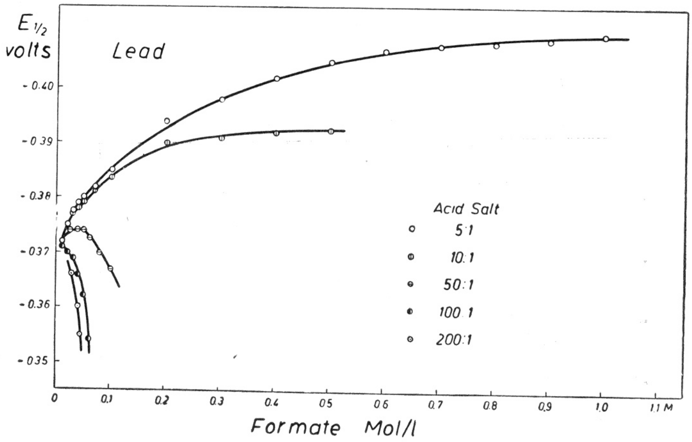


Fig. 4 Half-wave potential of lead *versus* formate concentration in buffers of acid-salt ratio: 5 : 1, 10 : 1, 50 : 1, 100 : 1 and 200 : 1.

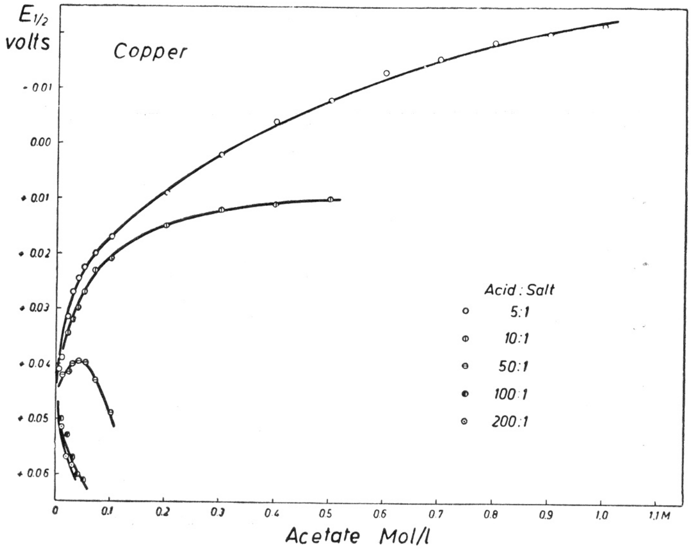


Fig. 5 Half-wave potential of copper *versus* acetate concentration in buffers of acid-salt ratio: 5 : 1, 10 : 1, 50 : 1, 100 : 1 and 200 : 1.

Buffers of a Constant Acid Concentration

Buffer solutions of a constant monocarboxylic acid concentration have been investigated polarographically in the concentration range of the acid from 0.1 to 2 *M*. Graphs in Figs. 6—8 show the results for cadmium in formate, acetate and butyrate buffers with a concentration of the acid 0.1, 0.5, and 2 *M*. The curves representing the dependence of the half-wave potential on the monocarboxylate concentration have in general the same course for all three concentrations of the acid, *i.e.* the curves are almost parallel, especially those for an acid concentration of 0.1 M and 0.5 M. The ions of copper and lead give analogous graphs, as can be seen on Fig. 9 for copper in the formate buffer.

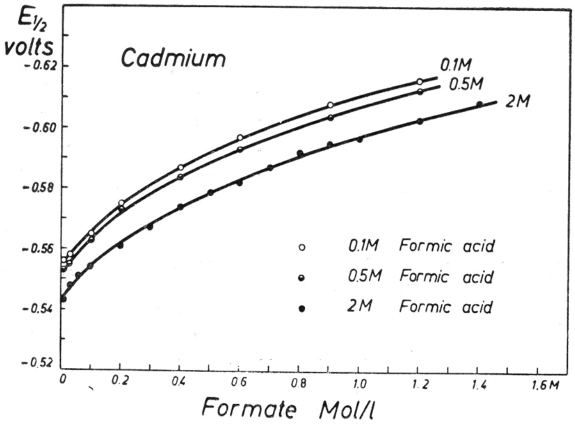


Fig. 6 Haf-wave potential of cadmium *versus* formate concentration in buffers of constant acid concentration: 0.1, 0.5 and 2 M.

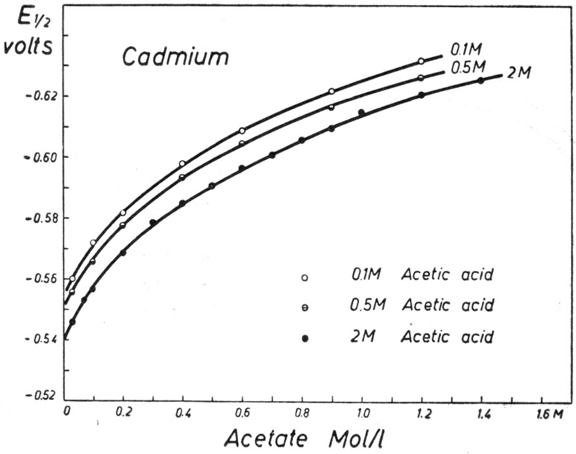


Fig. 7 Half-wave potential of cadmium *versus* acetate concentration in buffers with constant acid concentration: 0.1, 0.5 and 2 M.

The approximate parallelism of he curves representing the relation of half-wave potential and monocarboxylate concentration, points to the conclusion that the concentration of the monocarboxylic acid (in the interval from 0.1 to 2 M) has no bearing on the determination of the composition and the stability constants of the monocarboxylato complexes, the difference of the half-wave potential of the free (solvated) and the coplexly bound ion being the determinating factor. However, if the half-wave potentials of the free metal ions are determined by extrapolation to zero monocarboxylate concentration and the ratio of the difference of the half-wave potentials ($\Delta E_{1/2}$) and the concentration of the monocarboxylate is represented graphically, identical curves for all three acid concentrations are obtained only

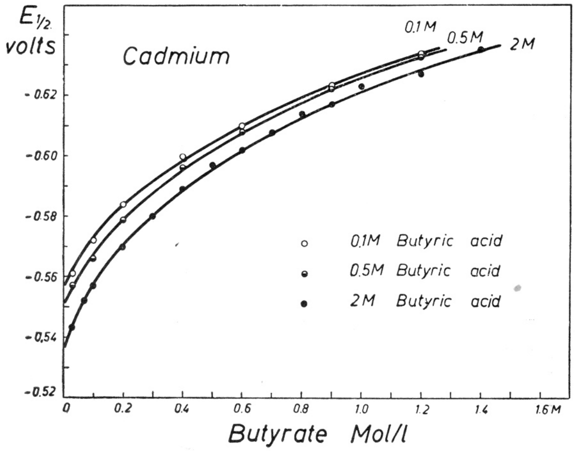


Fig. 8 Half-wave potential of cadmium *versus* butyrate concentration in buffers with constant acid concentration: 0.1, 0.5 and 2 *M*.

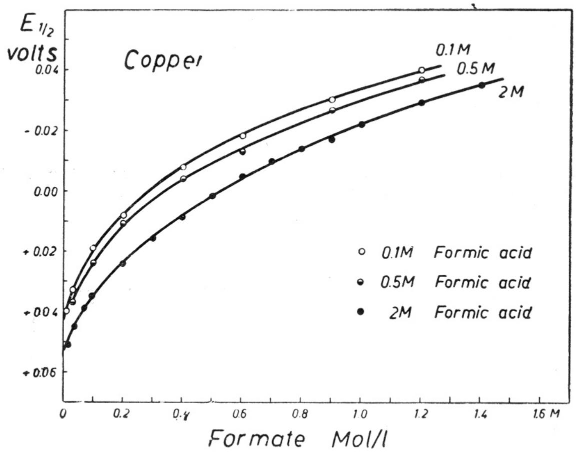


Fig. 9 Half-wave potential of copper *versus* formate concentration in buffers of constant acid concentration: 0.1, 0.5 and 2 *M*.

with formates. This can be seen in Fig. 10 for cadmium. In Fig. 11 curves for acetates show the deviation occurring when the concentration of the acid is 2 *M*. In the case of the butyrate buffer the curves differ in shape, as can be seen in Fig. 12. Generally it can be said that the steepness of the curve is increasing with the increase of the monocarboxylic acid concentration in the buffer. This increase is insignificant for formates, but is becoming more pro-

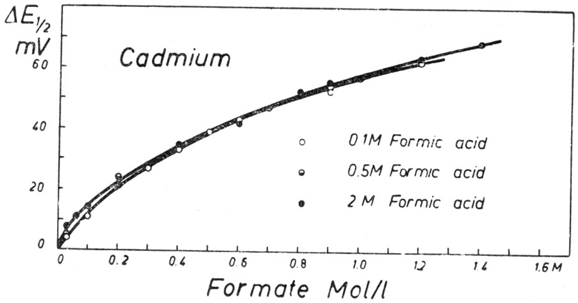


Fig. 10 Half-wave potential difference between the free and complex cadmium ion *versus* concentration of formate in buffers of constant acid concentration: **0.1, 0.5** and **2** ***M.***

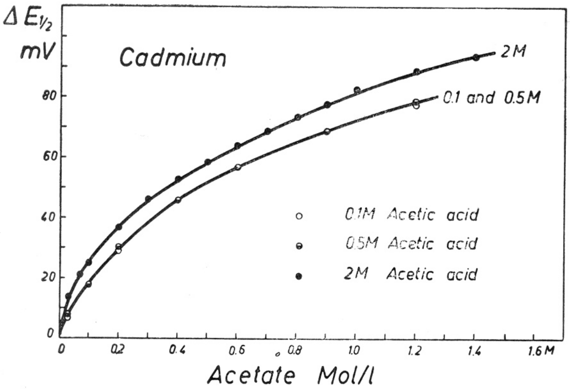


Fig. 11 Half-wave potential difference between the free and complex cadmium ion *versus* concentration of acetate in buffers of constant acid concentration: **0.1, 0.5** and **2** ***M.***

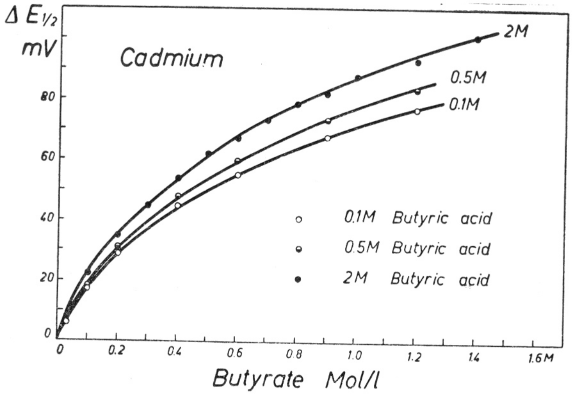


Fig. 12 Half-wave potential difference between the free and complex cadmium ion *versus* concentration of butyrate in buffers of constant acid concentration: **0.1, 0.5** and **2** ***M.***

nounced from acetates to butyrates. It must be stressed, however, that a greater steepness of the curve for higher acid concentrations is another proof for the conclusion that no hydrolysis of the monocarboxylate complexes occurs in lower acid concentrations, because if it was the effect would be exactly the opposite.

DISCUSSION

The change of the half-wave potential of a certain metal ion can be caused by various factors[1]. From the Heyrovský-Ilkovič equation for the half-wave potential of a metal ion which is soluble in mercury and taking account of the liquid junction potential (E_j):

$$E_{1/2} = E_a{}^{\circ} + E_j + \frac{0.059}{n} \log \frac{f_i}{f_a} + \frac{0.059}{n} \log \left(\frac{D_a}{D_i} \right)^{1/2} \qquad (1)$$

it can be seen that when the amalgam formed at the dropping electrode is very dilute ($f_a = 1$), and when the diffusion coefficient of the metal atom in the amalgam is constant (D_a = const.), the half-wave potential depends on the liquid junction potential of the cell, the activity coefficient of the metal ion and the diffusion coefficient of the metal ion:

$$E_{1/2} = \text{const.} + E_j' + \frac{0.059}{n} \log f_i - \frac{0.059}{n} \log D_i^{1/2} \qquad (2)$$

According to the Stokes-Einstein diffusion equation[1], the diffusion coefficient depends on the viscosity coefficient (η) of the medium, if the radius of the particle is not changed ($[L]$ = const.), *i.e.* $D = \text{const.}/\eta$. Consequently:

$$E_{1/2} = \text{const.} + E_j' + \frac{0.059}{n} \log \eta^{1/2} \qquad (3)$$

if in E_j' the influence of E_j and f_i is included. Therefore the shift of the half-wave potential due to the change of the viscosity coefficient of the solution is:

$$\Delta E_{1/2} = \frac{0.059}{n} \Delta \log \eta^{1/2} \qquad (4)$$

Influence of the Change in the Viscosity of the Monocarboxylate Buffer

From equation (4) it appears that by increasing the viscosity of the buffer solution, the half-wave potential is shifted to more positive values. Changes of the half-wave potential ($\Delta E_{1/2}$) of Cd^{+2}, Pb^{+2}, Cu^{+2}, caused by the change of the viscosity coefficient, have been calculated for some buffer solutions in which a constant ionic strength 2 was maintained by addition of $NaClO_4$. The values are given in Table I.

As can be seen, the influence is somewhat more pronounced in butyrate buffers. For the rest of the buffers the changes are within limits of the experimental error. Naturally, for an univalent ion such as Tl^{+}, the value of $\Delta E_{1/2}$ is twice as large and the influence of the change of the viscosity of the solution is considerable, especially in butyrate buffers.

TABLE I

HL *M*	NaL *M*	Formate		Acetate		Butyrate	
		η	$\Delta E_{1/2}$ mV	η	$\Delta E_{1/2}$ mV	η	$\Delta E_{1/2}$ mV
0.1	0	1.153	0.1	1.154	1.0	1.205	2.2
2	0	1.172		1.350		1.713	
0.1	0.1	1.146	0.1	1.175	1.0	1.290	2.1
2	0.1	1.167		1.372		1.792	
0.1	1	1.203	0.1	1.353	1.2	1.651	2.5
2	1	1.222		1.623		2.450	

Influence of the Liquid Junction Potential and the Solvent

It is known that a very high liquid junction potential is obtained at the boundary of a solution in water with a solution in an organic or mixed solvent.[11] The same case arises in polarographic investigations of metal monocarboxylato complexes. Namely, of the two half-cells, one is the calomel electrode with a saturated sodium chloride solution, and the other contains the metal ion in the monocarboxylate buffer with a definite amount of organic solvent, *i.e.* monocarboxylic acid:

C. E.	NaCl (sat.)	$M(ClO_4)_2$ ($5\times10^{-4}M$) NaL HL $NaClO_4$	dropping mercury electrode

Accordingly, the positive shift of the half-wave potential with the increase of the monocarboxylic acid is caused primarily by the liquid junction potential, which is a function of the monocarboxylic acid concentration in the buffer. This is evident also from the measurements of half-wave potential of thallium(I) in formate and acetate buffers with a constant concentration of formic and acetic acid (Figs. 13 and 14). As the ion of thallium(I) does not form detectable complexes in acid solutions[7,12], from the measurements of its half-wave potential, E_j' can be determined as a function of the concentration of

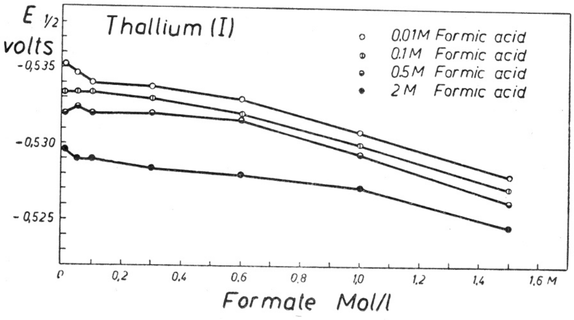


Fig. 13 Half-wave potential of thallium (I) *versus* formate concentration in buffers with constant acid concentration: 0.01, 0.1, 0.5 and 2 *M*.

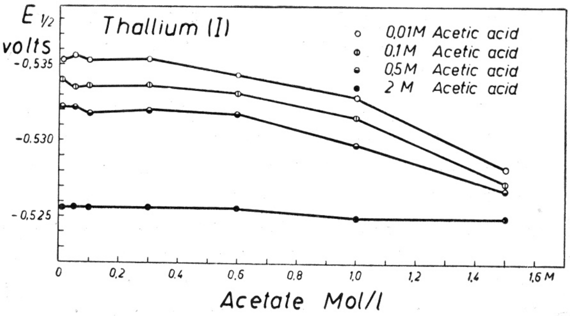
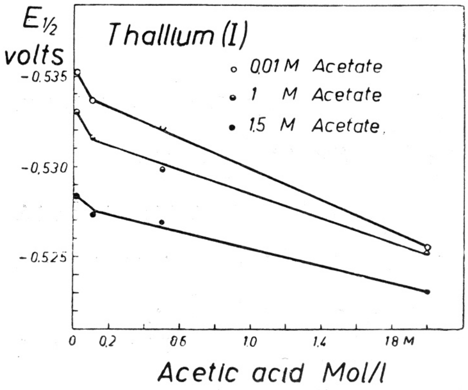


Fig. 14 Half-wave potential of thallium (I) *versus* acetate concentration in buffers with constant acid concentration: 0.01, 0.1, 0.5 and 2 *M*.

monocarboxylic acid. In Fig. 15 and 16 such measurements are represented for formate and acetate buffers. The half-wave potential increases towards positive values almost linearly with the molarity of the monocarboxylic acid in the range between 0.1 to 2 moles.

However, from Figs. 13 to 16 it appears that the half-wave potential of thallium(I) is shifted to more positive values not only with increasing concentration of the monocarboxylic acid but also with an icrease of the ligand in the buffer. The same effect exists presumably also in solutions of the other



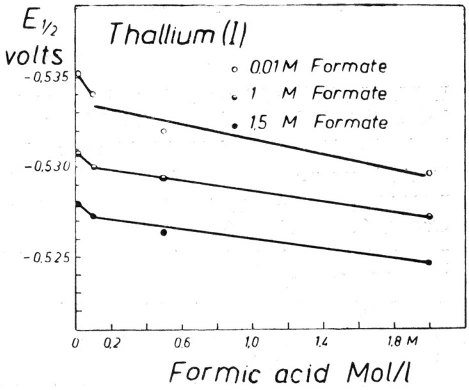


Fig. 15 Half-wave potential of thallium (I) *versus* formic acid concentration in buffers with constant formate concentration: 0.01, 1 and 1.5 *M*.

Fig. 16 Half-wave potential of thallium (I) *versus* acetic acid concentration in buffers with constant acetate concentration: 0.01, 1 and 1.5 *M*.

ions investigated (Cd^{+2}, Pb^{+2}, Cu^{+2}), but cannot be detected because of the negative shift caused by complex formation. Evidently, a variation of the liquid junction potential with the concentration of the ligand occurs, since the ligand is not a minor constituent of the ionic medium any more.[11] Besides, specific influences on the activity coefficients exist, in spite of the ionic strength being kept constant. These specific influences are caused not only by the change of the composition of the ionic medium (ionic interactions),[13] but also by a change of the composition of the solvent (ion-solvent interaction).[14] T. J. Lane, J. W. Thompson and J. A. Ryan[15] have found, for instance, a positive shift of the half-wave potential of Cd^{+2} in a mixed solvent containing 50% of ethanol and 50% of dioxane.

Therefore, since the influence of the monocarboxylic acid on the half-wave potential of the metal ion is opposite (shift to more positive values) to the influence of the complex formation (shift to more negative values), the polarographic investigations of metal monocarboxylato complexes can be carried out only in buffers of constant monocarboxylic acid concentration. The half-wave potential of the »free« metal ion can be determined under such conditions only by extrapolation to zero ligand concentration, because of the influence of the monocarboxylic acid. As a result the liquid junction potential cancels out in calculations when taking differences of half-wave potentials. Other specific influences of thé medium remain, however, which are caused by the presence of the monocarboxylic acid in the buffer and a high concentration of the ligand. This is a reason for an uncertainty in the determination of the stability constants. Besides, the higher the concentration of the monocarboxylic acid in the buffer (a higher concentration being necessary for ions which hydrolize), the more uncertain the extrapolation of the half-wave potential. This is especially true for ions forming more stable complexes, *e. g.* indium. A further difficulty arises in the case of irreversible electrode processes at low monocarboxylate concentrations, *e. g.* with zinc. For all these reasons investigations were undertaken to find the best conditions for the application of the polarographic method in the determination of stability constants of the monocarboxylato complexes.

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IZVOD

Polarografska istraživanja monokarboksilato-kompleksa nekih metala. IV. Utjecaj monokarboksilne kiseline na poluvalni potencijal metalnog iona

I. Filipović i I. Piljac

Ustanovljen je utjecaj monokarboksilne kiseline (mravlje, octene i butirne) na poluvalni potencijal metalnog iona u monokarboksilatnom puferu. Kako je taj utjecaj upravo suprotan onom zbog kompleksnog vezanja, potrebno je istraživati monokarboksilato-komplekse u puferima s konstantnom koncentracijom kiseline, a ne u puferima konstantnog odnosa soli i kiseline. Pomicanje poluvalnog potencijala prema pozitivnijim vrijednostima s porastom koncentracije monokarboksilne kiseline u puferu uzrokovano je promjenom difuzionog potencijala, koeficijenta aktiviteta iona kao i promjenom viskoziteta otopine.

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